GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

Date: 12/16/80

Project Title: Emulsion Polymerization Kinetics and Continuous Reactors

Project No: E-19-637

Project Director: Dr. G. W. Poehlein

Sponsor: National Science Foundation; Washington, D. C. 20550

Agreement Period: From 11/15/80 Until 4/30/83 (includes usual 6 month unfunded flexibility period)

Type Agreement: Grant No. CPE-80114~~23~~ 55

Amount: $114,480 NSF
3,000 GIT (E-19-354)
$117,480 TOTAL

Reports Required: Annual Progress Reports; Final Project Report

Sponsor Contact Person (s):

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Defense Priority Rating: None

Assigned to: Chemical Engineering (School/~~Laboratory~~)

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GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

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SPONSORED PROJECT TERMINATION SHEET

Date 10/6/83

Project Title: Emulsion Polymerization kinetics and Continuous Reactors

Project No: E-19-637

Project Director: Dr. G.W. Poehlein

Sponsor: National Science Foundation

Effective Termination Date: 4/30/83

Clearance of Accounting Charges: 4/30/83

Grant/Contract Closeout Actions Remaining:

- [ ] Final Invoice and Closing Documents
- [x] Final ~~Fiscal Report~~ Accounting Report FCTR
- [x] Final Report of Inventions if positive
- [x] Govt. Property Inventory & Related Certificate
- [ ] Classified Material Certificate
- [ ] Other ______

Assigned to: Chem Engr (School/~~Laboratory~~)

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FORM OCA 10:781

TECHNICAL PROGRESS REPORT

NSF GRANT NO. CPE-8011455

TITLE: Emulsion Polymerization Kinetics and Continuous Reactors

PRINCIPAL INVESTIGATOR: Dr. Gary W. Poehlein

GRADUATE RESEARCH ASSISTANTS: Mr. Shini Higashida (M.S. candidate)
Mr. Hsueh C. Lee (Ph.D. candidate)
Mr. Lars Jansson (M.S. candidate)

UNDERGRADUATE RESEARCH ASSISTANT: Mr. Walter Dubner

REPORT:

Period Covered: 11/1/80 through 9/1/81

(1) Summary:

Research is underway in the three areas indicated below:

i. Modeling of emulsion polymerization in a seed-fed continuous stirred-tank reactor.

ii. Construction of a batch reactor system and the completion of preliminary batch reaction experiments.

iii. Design and preliminary construction of a continuous reactor system.

Preliminary plans are also being developed to study the kinetics of new high-swelling particles in continuous reactors. These particles were developed by John Ugelstad (Norway). Dr. Ugelstad visited Georgia Tech in April 1981 and we expect to collaborate on the use of the high-swelling particles in a CSTR. These seed particles could yield latexes with particle size distributions quite different from those resulting from standard emulsion polymerization recipes.

(2) Results:

i. CSTR Modeling: The first stage of the continuous reactor studies has involved the development of a rather general model for the steady-steady isothermal operation of a seed-fed CSTR. This work has progressed well and a rather complete paper is attached to this report. In summary, the model permits the prediction of polymerization rate and the particle size distribution of the product latex when the CSTR fed stream contains a monodisperse seed.

The model accounts for free radical transport into and out of the growing polymer particles and for radical termination in the aqueous phase. The model can serve several purposes. First, and most important with regard to this research, the model will provide a firm basis for planning the experimental portion of our research program. Second, assuming the model is successful, it can be used for process design and development. Third, the model can be used in fundamental kinetic studies to determine kinetic constants associated with radical transport and water-phase termination.

Some of the preliminary results are very interesting. Particle size distributions, calculated for the case where transport of free radicals out of particles is important, can be bimodal. In the past, such distributions have been attributed to transient particle formation phenomena. It was not believed possible to generate bimodal distributions with state-state operation.

A second, and related factor, is that small changes in the parameter used to quantify radical desorption has a major influence on the nature of the latex particle size distributions. Thus good measurements of these distributions should permit accurate evaluation of radical desorption kinetic parameters.

ii. Batch Reactor Studies: A batch reactor system has been constructed and the following experiments have been carried out.

a. A series of monodisperse polystyrene latexes have been produced with particle sizes ranging from about 50 nm to slightly more than 300 nm.

b. Continued-growth experiments have been carried out with some of these latexes; both without and with added chain transfer agents.

c. Competitive growth experiments have been conducted with the monodisperse latexes, with and without chain transfer agents.

d. Experiments have been started to produce monodisperse latexes with other monomers. Our first experiments have been with methyl methacrylate.

The most important results of these preliminary experiments have been a demonstration that added transfer agents can reduce the rate of emulsion polymerization. These same transfer agents are reported to have no influence on polymerization rates in solution or bulk polymerization. Hence the transfer reactions must influence the rate by increasing the rate of transfer of free radicals out of the latex particles.

iii. Construction of Continuous Polymerization System: The experimental continuous polymerization system has been designed, some equipment has been obtained and the remaining equipment is currently being placed for bids. Some construction associated with the support and fluid flow systems has been completed. The continuous flow system will permit operation with and without a continuous tubular prereactor. Mean residence times in the CSTR can be varied from less than 10 minutes to more than 60 minutes.

System instrumentation will permit continuous monitoring of latex density (related to reactor conversion and polymerization rate) and latex surface tension. This will permit accurate data logging and will allow for eventual closed loop control of the reactor.

iv. Reactions with High Swelling Particles: Most latex particles comprised of high molecular weight polymer are swollen with momomer by a volume factor of 2 to 4. Ugelstad and coworkers, however, have developed techniques for preparing particles which will swell by factors of 100 to 1,000. To date, emulsion polymerization experiments with these particles have been restricted to batch reactors. A number of interesting questions can be raised with regard to how highly-swellable seed particles would polymerize in a CSTR. We have begun preliminary discussions with Dr. Ugelstad on possible use of his particles in our reactor systems.

(3) Problems and Developments:

The major problem in starting the research was a lack of qualified graduate students. We now have three graduate students and one undergraduate working on emulsion polymerization problems. I hope to add one other student before January 1982. Some of these students are supported by Institute funds.

The most significant developments on the current research program are listed below:

i. Model predictions for a seed-fed CSTR system clearly demonstrate that a bimodal particle size distribution can be produced under steady-state operation. In the past such distributions have been attributed to cyclic operation.

ii. Chain transfer agents which do not influence the rate of bulk or solution polymerization have been shown to slow the rate of emulsion polymerization. This is because chain transfer reactions increase the rate of radical desorption from the polymer particles.

(4) Future Work:

Experimental and theoretical work will proceed in several areas during the next year. The most important research plans are outlined below.

i. CSTR Modeling: The present model has been developed for a feed stream of monodisperse particles. Future work is required in the following areas.

a. Parameter Evaluation: The model development involves dimensionless parameters that account for all of the major kinetic and reactor variables. Preliminary computations have demonstrated the general trends of reactor performance as influenced by these parameters. A much broader and more detailed model study will be completed during the next year.

b. Seed Distributions: The present model is based on a feed stream of monodisperse seed particles. Since some seed latexes would have a broad particle size distribution, we plan to alter the model to include the possibility of dealing with any seed size distribution. This model change will also permit us to handle calcuations for multiple reactors connected in series; a common industrial reactor system.

c. Parameter Evaluation: Past model calculations have been based on the assignment of reasonable values to the various kinetic parameters associated with emulsion polymerization reactions. We eventually will want to turn this process around and evaluate the kinetic parameters from experimental data. Particle size distributions and polymerization rates will be determined experimentally and these measurements will be used to determine kinetic parameters. Of particular interest will be the parameters associated with radical desorption from particles and with water-phase termination.

ii. Batch Reactor Studies:

Polymerizations carried out in batch reactors can be complimentary to the CSTR work. Some of our research plans with batch systems are described below.

a. Experimental Work: We plan to continue experimental work with batch reactors in several areas. Styrene emulsion polymerizations will be carried out with and without added chain transfer agents. The use of chain transfer agents will permit a more detailed analysis of radical desorption. Competitive growth experiments will also be completed. These experiments start with mixtures of two or three seed particles. The relative growth rates can be measured and used to examine kinetic mechanisms. Other experiments will be carried out with different monomers such as methyl methacrylate and vinyl acetate.

b. Reaction Modeling: Models will be developed for seeded batch reactor systems that will permit us to calculate the course of the reaction as a function of the important kinetic parameters. These models will then be used to evaluate kinetic mechanisms from the batch reactor experimental data.

iii. CSTR System: Construction of the continuous reactor system will be completed and a number of preliminary experiments carried out. The reactor system will permit operation with a single CSTR or with a continuous tubular reactor connected up-stream of a single CSTR. The experimental parameters to be studied will include:

a. Recipe Ingredients; monomers, initiators, emulsifiers and chain transfer agents. Both type of ingredients and their concentrations need to but studied, but not all of these variables can be examined in one year.

b. Reactor operation such as mean residence time and/or reactor conversion. When the pretubular reactor is used, the nature of the product latex will be varied--i.e., the latex particle size and number.

The continuous reactor system will be instrumented for on-line measurement of temperature, reaction conversion and surface tension. These measurements will permit us to follow potential reactor transients and they will be used to establish the existance of steady-state operation.

iv. High-Swelling Particles: We have just begun to study the potential of using high-swelling seed particles in a CSTR system. These particles, which can swell with monomer by a factor of 1,000, have been used in batch reactors to produce large latex particles--sometimes as large as 50 microns in diameter. Batch experiments have involved particles of nearly the same size and polymer concentration. A number of interesting questions can be raised about the possibility of using a CSTR system with the high-swelling seed particles:

a. What will be the swelling differences among particles of different sizes which contain different amounts of high and low molecular weight polymer?

b. What kind of particle size distributions will be formed in a single CSTR?

c. Will the system of particles be in thermodynamic equilibrium or will mass transfer effects be important?

If time permits, and if we can attract another student, some of these questions will be explored.

(5) Presentations and Publications:

The following presentations and papers have been based, in part, on work done under the present grant.

i. Presentations at DeSoto, Inc., Des Plaines, Ill. (May 8, 1981), "Emulsion Polymerization in Continuous Emulsion Polymerization Systems--Problems to be Considered for Commercial Development."

ii. Presentations (2) at Lehigh University Short Course on Emulsion Polymers (June 8 and 9, 1981), "Emulsion Polymerization Kinetics" and "Continuous Emulsion Polymerization."

iii. Presentation at SUNY at New Paltz Short Course on Advances in Polymer Synthesis, Modification and Characterization (June 19, 1981), "Progress in Emulsion Polymerization."

iv. Presentations (3) at Davos, Switzerland. Short Course on Emulsion Polymers (August 17-21, 1981), "Principles of Polymer Reactor Design," "Emulsion Polymerization Mechanisms and Kinetics," and "Continuous Emulsion Polymerization."

v. Presentations (2) at London, England Symposium on Continuous Emulsion Polymerization (September 24, 1981), "Continuous Emulsion Polymerization--A General Review" and "Use of Seed Particles in the Feed Streams of CEP Reactors."

vi. Paper (Prelimary Draft) of a paper entitled, "Steady-State Analysis of Emulsion Polymerization in a Seeded, CSTR," by Gary Poehlein and Walter Dubner. A copy of this preliminary paper is attached for NSF files. This paper will be submitted for publication after a little broader parameter evaluation has been completed.

vii. Book Chapter entitled, "Emulsion Polymerization in Continuous Reactors," will be published in a book, Emulsion Polymerization, edited by I. Piirma. The book will be published by Academic Press in 1982. A copy of the corrected galley proofs is attached for NSF Files.

NATIONAL SCIENCE FOUNDATION
Washington, D.C. 20550

FINAL PROJECT REPORT
NSF FORM 98A

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PART I—PROJECT IDENTIFICATION INFORMATION

1. Institution and Address	2. NSF Program	3. NSF Award Number
Georgia Tech Research Institute Georgia Institute of Technology	Chem. & Biochem Processes	CPE-8011455
	4. Award Period From 11/15/80 To 4/30/83	5. Cumulative Award Amount $114,480

6. Project Title
Emulsion Polymerization Kinetics and Continuous Reactors

PART II—SUMMARY OF COMPLETED PROJECT *(FOR PUBLIC USE)*

The kinetics of emulsion polymerization reactions and their use in reactor development and design is important for many commercial products including synthetic rubbers, coatings, adhesives, additives for textile and paper products, flocculation chemicals and scientific colloids. The primary objective of this research project was to study the kinetics of emulsion polymerization in a continuous reactor system comprised of pre-tubular reactor followed by a continuous stirred-tank reactor (CSTR). The tube-CSTR system was chosen for two reasons. First, this reactor combination avoids the problem of particle nucleation oscillations often observed with CSTR systems and high production rates can be achieved. Second, the experimental data from tube-CSTR systems can be used for accurate determination of unknown reaction constants.

A rather general steady-state model has been developed for the tube-CSTR system. This model has been used to predict reactor performance and to analyze data for a seed-fed CSTR. The results demonstrate that transport of free radicals out of latex particles can have a dramatic influence on the particle size distribution (PSD) of the product latex. Thus we have used PSD measurements to determine model parameters for the radical transport mechanism.

Kinetic studies have also been carried out in batch reactors. Part of this work involved the measurement of polymerization rates and competitive growth of different size particles when transfer agents are present. The second part involved preliminary studies of latexes which are highly swollen (monomer:polymer ratios greater than 10:1) with monomer.

PART III—TECHNICAL INFORMATION *(FOR PROGRAM MANAGEMENT USES)*

1. ITEM *(Check appropriate blocks)*	NONE	ATTACHED	PREVIOUSLY FURNISHED	TO BE FURNISHED SEPARATELY TO PROGRAM: Check (✓)	Approx. Date
a. Abstracts of Theses		✓	✓		
b. Publication Citations		✓	✓		
c. Data on Scientific Collaborators	✓				
d. Information on Inventions	✓				
e. Technical Description of Project and Results			✓		
f. Other *(specify)* Two detailed progress reports dated 9/1/81 and 4/1/83.			✓		

2. Principal Investigator/Project Director Name *(Typed)*	3. Principal Investigator/Project Director Signature	4. Date
Gary W. Poehlein		6/10/83

Abstract

Swelling and Polymerization

of

Latex Particles

Lars Henning Jansson

98 pages

Directed by Dr. G. W. Poehlein

The purpose of this research was to obtain a better understanding of the mechanisms and conditions for swelling of seed particles with monomer. The goal was to produce narrowly distributed polystyrene particles in the size range of one to two micrometers diameter by polymerization of a latex containing highly swollen seed particles.

A model was developed and used for calculating the rate of diffusion of monomer between particles of defined composition, and for evaluating the final equilibrium condition for the particles. The equilibrium swelling capacity of monomer into polymer particles is predicted by the model to increase if the droplet size of monomer added to the seed particles is smaller than or near to the size of the seed particles. The model prediction was realized experimentally by homogenizing a styrene emulsion and adding it to monodisperse polystyrene seed particles (0.49 μm). A swelling ratio (volume monomer

to volume polymer) of about 14:1 was obtained.

Different high-swelling techniques and reactor systems have been studied experimentally. A swelling agent, comprised of a short-chained oligomer, has been used to increase the swelling capacity. Problems with new particle nucleation have been observed in these experiments and been analyzed.

A high-swelling experiment in a semi-continuous reactor system, where monomer was added continuously during the polymerization of monodisperse polystyrene particles preswollen with swelling agent (1-chloradodecane), kept a narrow particle size distribution throughout the reaction indicating an interesting alternative reactor set up for carrying out such high swelling reactions.